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Optical gain of CdS quantum dots embedded in 3D photonic crystals

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Abstract

Three-dimensional photonic crystals used in this study were synthetic opals, composed of submicron silica spheres, close-packed in a face-centered cubic lattice with a period of 200 nm, which exhibit a photonic gap around 600 nm. We report on the first observation of optical gain enhancement in semiconductor quantum dots embedded in a photonic crystal caused by modifications of light–matter interaction at the edges of the photonic gap. © 1998 Elsevier Science S.A.

Keywords: Photonic band gap materials; Semiconductor quantum dots; Optical gain; Lasing

1. Introduction

In recent years, a great attention has been paid to fabrication and study of photonic crystals, i.e., three-dimensional (3D) periodic dielectric structures with periodicity matching the optical wavelength, which can possess photonic band gaps (PBG), namely, the frequency stop-bands in which the density of photonic states tends to zero [1]. Redistribution of the photonic modes in the vicinity of PBG can result in a total suppression or enormous enhancement of the spontaneous emission rate of the active media, placed within the photonic crystal. The emission spectra of an active media placed within a photonic crystal should be, therefore, drastically altered, which may play an important role in low threshold of microlasers based on photonic band gap engineering [1,2] (for a recent review, see articles in Ref. [3]). To obtain a 3D photonic crystal, however, with submicron lattice constant for operating in visible region of spectra, still remains the challenging question. Recently, it was found that synthetic opals, composed of submicron silica a-SiO_2 spheres, closely packed in a 3D face-centered-cubic (FCC) structure with a period of about 200 nm, possess photonic stop-bands throughout the visible spectrum (400–600 nm) [4–6]. According to numerous theoretical calculations of the photonic band structure of opal-like FCC photonic lattices composed of spherical 'atoms' [7], an absolute PBG with zero density of photonic states (DOS) between the lowest photonic zones is prohibited by symmetry restrictions. It is possible, however, to expel the propagating photonic modes along all but a few directions, thus creating a very large depletion of photonic DOS—a 'pseudogap'. Although the DOS in this case is finite, however, almost all the optical phenomena predicted for photonic crystals possessing an absolute PBG should occur in a 'pseudogap' crystal as well. Recently, it was shown that the 'pseudogap' criterion can be met in opals by impregnating the interstitials between the silica spheres with a high refractive index semiconductor [6].

2. Experiment and discussion

Our synthetic opal samples were fabricated by three subsequent technological procedures: sol–gel synthesis of monodisperse (standard deviation less than 3%) suspension of silica spheres, sedimentation of the suspension into a solid-state-ordered array followed by thermal annealing. The exposure of the porous opal matrices to a vapor flow of Cd and S results in a formation of wurtzite CdS nanocrystals of about 6 nm mean diameter [4,6], which fill homogeneously all the empty voids between the spheres. Transmission spectrum of the opal/CdS sample measured at normal incidence to the (111) face is presented in Fig. 1A in a semilogarithmic scale. Besides the drastic decrease of transmission at short wavelengths above 480 nm, due to

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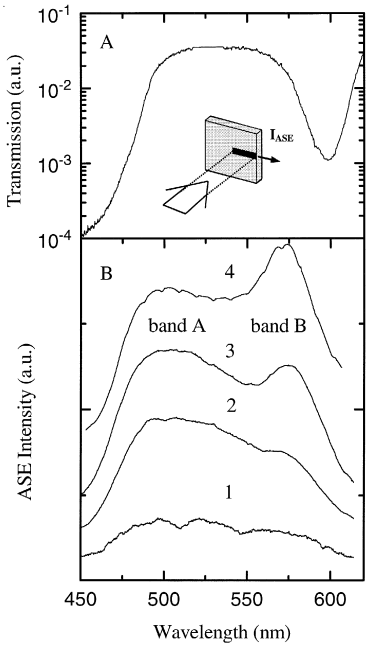

Fig. 1. (A) Transmission spectrum of opal/CdS sample taken at 10 K at an incidence normal to the (111) surface. (B) Set of ASE spectra measured at 10 K with 150 μm stripe length oriented along the ⟨211⟩ direction as a function of excitation intensity 1—0.25, 2—0.55, 3—0.77, 4—1 MW/cm^2. Inset: Geometry of VSL experiment.

the absorption of light in semiconductor nanocrystals, the large drop centered at 600 nm can also be clearly seen. It is ascribed to a photonic stop-band at the point L of the photonic Brillouin zone (BZ) [4–6].

For high-intensity excitation in our optical gain measurements, a XeCl-excimer laser emitting UV light pulses (308.5 nm) of 20 ns duration at 5 Hz repetition rate is used. The optical gain is measured with the variable-stripe-length (VSL) method [8]. The laser beam is focused onto the (111) face of the sample in the form of a narrow rectangular stripe, having a width of about 20 μm and a variable length D. The emitted light (i.e., amplified spontaneous emission (ASE)) is collected from the cleaved edge of the sample in the direction of the stripe. Fig. 1B represents a set of ASE spectra measured at 10 K in the stripe direction for a fixed stripe length of $D = 150$ μm as a function of the excitation intensity. At low pumping, the spectrum consists of a single broad band (band A) with its maximum at 500 nm and a very wide tail extending to longer wavelengths (see spectrum 1 in Fig. 1B). It can be seen (spectra 2–4) that an increase of pumping results in the appearance of a well-defined long wavelength band centered at 570 nm (band B). The presence of two emission bands is typical for photoluminescence spectra of QDs in glass [9], which are usually ascribed to intrinsic excitonic recombination (short-wavelength band) and to a recombination related to defect or surface states (long-wavelength band). Note, however, that the defect-related band is typically very broad (about 200 nm FWHM) and is centered in the near-infrared region at 650–700 nm [9]. Unlike this, the band labeled B observed in our opal/CdS sample is centered at shorter wavelengths, and its width is much smaller (about 50 nm FWHM). Moreover, the band B increases faster with excitation intensity than the band labeled A in Fig. 1B. It does not saturate even at the highest excitation intensities used. This behavior is opposite to that usually observed in CdS QDs in a glass matrix for defect-related long-wavelength band [9]. It can be supposed that this band originates from the same intrinsic states as band A, but the long-wavelength portion of its spontaneous emission is greatly amplified due to the interference effects in the 3D photonic lattice.

To verify this hypothesis, the optical gain measurements were performed at various excitation intensities and for different temperatures. The effective gain coefficient g (total gain minus losses) can be obtained by fitting the $I_{ASE}(D)$ dependence using the expression [8] $I_{ASE}(D) = A/g \cdot (\exp(g \cdot D) - 1)$, where A is a spontaneous emission intensity constant. The value of $g = 220$ cm^{-1} was obtained by fitting $I_{ASE}(D)$ measured at the maximum of band A for 1 MW/cm^2 excitation, which is comparable to that observed in CdS QD in glass matrices for a similar temperature and excitation intensity [9]. The gain diminishes as the intensity of excitation I_p is reduced and it practically disappears at 0.2 MW/cm^2. The $g(I_p)$ dependence reveals a quadratic increase of gain with increasing excitation intensity. This behavior is expected for the gain processes involving two electron-hole pairs (biexciton) recombination.

In parallel with gain measurements taken at 500 nm wavelength (Fig. 2A), the gain is measured also at longer wavelengths. It was found that the gain measured at the

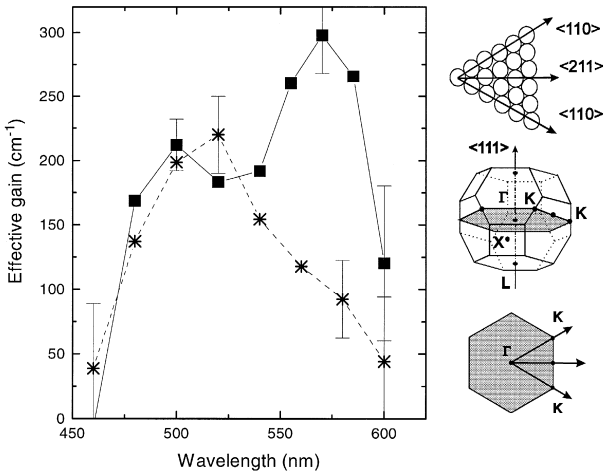

Fig. 2. Gain spectra measured at 10 K for 1 MW/cm^2 excitation intensity for the stripe oriented along the ⟨211⟩ direction (squares) and along the ⟨110⟩ direction (stars). Inset: Sketch of spheres packaging on the (111) face of the sample, corresponding photonic BZ, and its projection on the (111) plane. The arrows in each of sketches mark two directions of ⟨211⟩ and ⟨110⟩ type, along which the stripe is oriented in our VSL experiments.

maximum of band B at 570 nm far away from the absorption edge is surprisingly large. Moreover, for our maximum excitation intensity of 1 MW/cm^2, it reaches the value of $g = 300$ cm^{-1}, which is nearly 1.5 times larger than $g = 220$ cm^{-1} measured for band A. It can be supposed that this long-wavelength gain, which is quite unusual for QD in glass, results from some type of modifications of light–matter interactions in a 3D photonic crystal [1,3,2]. If this is the case, then the band B emission should possess well-defined directional properties according to the symmetry of photonic lattice of the dielectric opal matrix. Indeed, the (111) face of the opal photonic lattice, onto which the stripe is focused in the VSL gain experiments, possesses two inequivalent directions (⟨110⟩ and ⟨211⟩, see inset in Fig. 2), which can be clearly identified by the analysis of the AFM images. For the ⟨110⟩-oriented stripe, the wavevector $\boldsymbol{k}$ of photons, which are collected in the VSL method in the stripe direction, increases in Γ–K direction in photonic BZ. When $|\boldsymbol{k}|$ approaches the boundary of the first BZ at point K with coordinates $2\pi/a^*(3/4,3/4,0)$ (see inset in Fig. 2), the photonic stop-band develops. The photonic stop-band for the ⟨211⟩ direction should occur at longer wavelengths, since the magnitude of the wavevector $|\boldsymbol{k}|$, which corresponds to the boundary of BZ in the ⟨211⟩ direction, is about 10% smaller than that to point K (see inset in Fig. 2). Point L is the closest to the center of BZ; therefore, corresponding stop-band is centered at the longest wavelengths. These expectations were confirmed recently by direct mapping of photonic band structure of synthetic opals [5].

In all the gain measurements described above, the stripe was oriented along one and the same ⟨211⟩ direction. The measurements of the orientation dependence of the gain were performed by rotation of the sample around the [111] axis, which is perpendicular to the sample base surface. Fig. 2 depicts gain spectra measured for ⟨211⟩ (squares) and ⟨110⟩ (stars) oriented stripes for one and the same excitation intensity of 1 MW/cm^2 at 10 K. It can be clearly seen that band B dominates in the gain spectra only for stripes oriented along the ⟨211⟩ direction. Rotation of the sample around the [111] axis by only 30° (the stripe is then oriented along the [110] direction) results in a blueshift and disappearance of band B, as expected.

3. Conclusions

In conclusion, optical gain was observed for the first time in semiconductor nanocrystals embedded in a 3D photonic crystal. The gain spectrum exhibits two regions, one of which develops near the semiconductor absorption edge and originates from the quantum-confined states involving biexciton to exciton transitions. Another gain region at energies far below the semiconductor absorption edge is caused by enhancement of the long-wavelength portion of the gain defined by light interference in the 3D photonic lattice. Well-defined spatial directionality of ASE at band B, exponential increase of its intensity with a threshold pumping value, relatively small spectral width allow to talk about the first observation of lasing action in a semiconductor placed within a 3D photonic crystal, which occur without recourse to any external mirrors or cavities. Several mechanisms, predicted to occur in 3D photonic crystals, can be responsible for the observed effect [1,3,2]. We hope that further studies of the gain kinetics, which are under way now, will allow distinction between them. We would like to note at this point, that accounting for even one of the proposed mechanisms, caused by slowing down of the photon group velocity at the photonic band edge, which implies an exceedingly long optical path length in the structure [2], may explain the observed magnitude of gain enhancement.

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